PREPARATION OF A NEW ORGANIC HETEROCYCLIC LUBRICATING ADDITIVE AND ITS FRICTION AND WEAR PERFORMANCES ON THE STEEL/STEEL FRICTION PAIR

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A new kind of organic heterocyclic lubricating additive was prepared and the structure of it was characterized by elementary analysis, FT-IR and ^{13}C-NMR spectroscopy. Its tribological behaviour in liquid paraffin were evaluated on the common steel/steel friction pair by the four-ball tester and universal friction & wear testing machine. And the topographies and chemical characteristcs of the worn surfaces were investigated by means of optical microscope, scanning electron microscope and X-ray photoelectron spectroscopy. The results indicated that the prepared lubricating additive could obviously reduce the wear loss of the steel/steel friction pair, enhance the maximum nonseizure load (P_B) and improve the anti-wear and friction-reduction properties of the base stock, as might be mainly ascribed to the formation on friction surfaces of the composite boundary lubrication film with ferrous oxide and nitrogen-containing metallic chelate as main components, along with the occurrence of the tribochemical reactions during the rubbing process.

Keywords: Lubricating additive; steel/steel friction pair; anti-wear; friction-reduction

1. Introduction

Friction and wear are very common phenomena in nature. It’s estimated that 50%~70% of the world’s disposable energy is wasted due to the friction in mechanical movement, and 80% of the equipment damage is caused by all forms of wear [1]. Lubrication is an important technical measure taken to reduce the friction and wear. As a necessity for securing mechanical operation, lubricating

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oil has been called “industrial blood”. Lubricating additives, including inorganic ones [2-4] and organic ones [5-6], can be used to improve the anti-wear and friction-reduction property of lubricating oil and extend the service life of machinery equipment. Steel/steel friction pair is a mechanical friction pair widely applied in modern industry.

In recent years, with the continuous improvement of modern mechanical properties and the increasing reinforcement of environmental protection laws and regulations, new and high requirements have been raised on lubrication. For example, in order to avoid electrochemical corrosion, Arupt et al. [7] studied the lubrication of silver-containing alloy bearing and required the use of “Zinc-free” lubricating oil, Rokosz et al. [8] required that “low/zero- sulphur” or “low/zero-phosphorous” lubricating oil must be used in the unit to prevent the poisoning of three-way catalyst after studying the internal combustion engine installed with tail gas treatment unit. In this point, both of Arupt [7] and Spikes [9] et al. believed that conflicts between the increasingly strict emission regulations and the “low sulphur/low phosphorous” lubricating oil would continue or escalate. Now, the study of “ash-free/zero-sulphur/zero-phosphorous” organic lubricating additives has become one of the hot topics in the field. Numerous existing researches have proven that nitrogen-containing heterocyclic lubricating additives have high electronegativity with small atomic radius, compact molecular structure and the easy formation of hydrogen bonds between the molecules adsorbed onto the metal surface, leading to an increase in both of the lateral attraction and the oil film strength. With excellent tribological properties, a great number of organic nitrogen-containing heterocyclic lubricating additives have attracted wide attention [10-15]. However, as most of them contain sulphur or phosphorus in molecules, it required a great deal of in-depth research regarding the preparation, the tribological property and the function mechanism of the organic nitrogen-containing heterocyclic lubricating additive without sulphur and phosphorus.

A new organic nitrogen-containing heterocyclic lubricating additive without sulphur and phosphorus was prepared in this paper. In addition to studying its friction and wear performance on the steel/steel friction pair, its antiwear and friction-reduction mechanism was also analyzed by optical microscope (OM), scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS).

2. Experiments

2.1. Experimental materials

O-aminobenzoic acid is chemically pure and formamide, n-hexadecanoic acid, formaldehyde solution, sodium chloride, are all analytically pure.

2.2. Preparation of lubricating additive

155 grams of o-aminobenzoic acid and 177 grams of formamide were added into a beaker and heated for 3 h at 110～134 °C and 2 h at 160～170 °C. After the reaction, it was cooled down slowly. Then abundant water was poured in for the washing. After the grinding, filtering and drying in a mortar, white acicular crystal was obtained. It was then added with 1 liter of 1, 4-dioxane and 500 milliliter of formaldehyde solution, and heated for around 1 h at 50~80 °C until the solid was completely dissolved and the solution began to look clear. After the standing, filtering and drying, white acicular crystal was obtained once again, and it was added with an equivalent amount of n-hexadecanoic acid for the esterification reaction. Finally, white waxy solid was obtained, which was also the target product for lubricating additive.

2.3. Characterization of lubricating additive

Elemental analysis was performed by the Elementar Uario EL Ⅲ elemental analyzer (Germany); infrared analysis was performed by the Bio-Rad Win1725X FT-IR spectrometer (USA); and NMR analysis was performed by a Bruker AV300 NMR spectrometer made in Switzerland (TMS used as an internal standard).

2.4. Friction and wear property

The MQ-800 four-ball tester produced by Jinan Testing Machine Factory was used with the maximum nonseizure load (P_B) having been evaluated by the China national standard of GB3142-82 under the following test conditions: the ambient temperature around 20 °C, the rotational speed 1500 rpm, the use of standard experimental Grade II GCr15 steel balls, ϕ12.7 mm and 59～61 HRC hardness. The base oil was the analytically pure liquid paraffin (with a kinematic viscosity of 21.20 mm^2/s at 40 °C).

The vertical universal friction & wear testing machine MMW-1P can evaluate the tribological performances of lubricants, metals, plastics, coatings, rubber, ceramics and other materials in the friction form of rolling, sliding or rolling/sliding composite motion under certain load, low speed or high speed conditions, which was used to study the anti-wear and friction-reduction property of the steel-steel friction pair through the point-contact and surface-contact tribological test according to the China petrochemical industry standard of SH/T 0189-05 and SH/T 0762-05. The point-contact test conditions were: the ambient temperature around 20 °C with the steel balls the same with those used in the above-mentioned P_B test, the rotational speed 1500 rpm, a wear time of 30 min, the measurement of the wear scar diameter (WSD, the average value of the wear scar diameters of the three lower balls was adopted as the test value) and the friction coefficient under different working conditions. The friction pair contact mode of the surface contact was the sliding motion form of the disc-shaped friction pair, namely, the thrust ring friction pair. The surface-contact test conditions were: the ambient temperature around 20 °C, 45# steel (quenched) as the friction pair material, 45 HRC hardness, the relative speed of motion 800 rpm, the additive concentration 1％, gradually loaded at each load level of 98 N and the load-time of 98 N-30 min, 196 N-15 min, 294 N-15 min, 392 N-15 min and 490 N-15 min, respectively, and the measurement of the friction coefficient under different load levels.

2.5. Surface analysis

The Motic B5-223IPL OM (China) and JSM-6460LV low vacuum SEM (Japan) were used to observe the worn surface morphology of the specimen. The Thermo ESCALAB- 250 XPS (USA) was used to analyze the distribution, the composition and the state of the chemical elements on the worn surface of the specimen. The following test conditions: the double-anode Al-Kα line (300 W), the 1×10^{-8} Pa vacuum degree, the passing energy 50 eV, the residence time of 50 ms and the electron binding energy 284.6 eV of the contaminant C1s used as an internal standard. Before the analysis, the to-be-tested specimen was washed in petroleum ether with ultrasonic cleaning for 5 min.

3. Results and Discussion

3.1. Additive structure

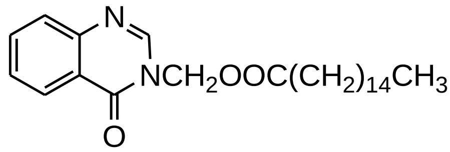
The experimental results obtained after the elemental analysis, IR and NMR spectroscopy analysis of the additive were given in Table 1.

Table 1

The experiment results of Elemental Analysis, FT-IR and ^{13}C--NMR

Elemental Analysis: $C_{25}H_{38}N_2O_3$		
Item	The measured value, %	The calculated value, %
C	72.64	72.46
H	8.92	9.18
N	6.51	6.76
FT-IR (KBr)		
Functional group	The wave number, cm^{-1}	
ν: C=O	1731	
ν: C=N	1613	
ν: C—N	1172	
ν: C—O	1099	
ν: ArH	3032	
ν: CH_2, CH_3	2954～2871	
ω: CH_2	1472	
γ: $(CH_2)n$, n>4	720	
^{13}C--NMR ($CDCl_3$, 300MHz)		
Functional group	The chemical shift, ppm	
1C, —CH_2CH_3	14.2	
14C, —$(CH_2)_{14}$—	24.7～34.1	
1C, ArCON—CH_2—OOC—	65.7	
1C, ArN=CH—N	147.6	
1C, —CH_2COOCH_2—	163.3	
1C, ArC—CO—N—	179.9	
6C, 	121.0～144.9	

Elemental analysis can detect the content of main elements in lubricating additives; FT-IR analysis can identify the chemical bonds and functional groups contained in the molecules of lubricating additives; ^{13}C-NMR spectroscopy can analyze the molecular structure of lubricating additives. Hence, the table above can prove that this organic nitrogen-containing heterocyclic additive has the structure as indicated below.



3.2. Friction and wear performances

3.2.1. Anti-wear property

As an indicator to evaluate oil film strength during boundary lubrication, maximum nonseizure load (P_B) can reflect the wear degree of the friction surface, so it shows the severity of the friction condition to some degree. Fig. 1 illustrates the change of the maximum nonseizure load against the concentration on the MQ-800 four ball tester.

As shown in Fig. 1, the maximum nonseizure load was significantly improved, after the lubricating additive had been added into the blank base oil. With 1.0% addition, the maximum nonseizure load could reach up to 530 N, which was improved by 80% compared to the load of 294 N in the blank base oil. However, with the increase of the concentration, the growth of the maximum nonseizure load was not obvious, which means that the adsorption of the lubricating additive on the metal surface was reaching saturation.

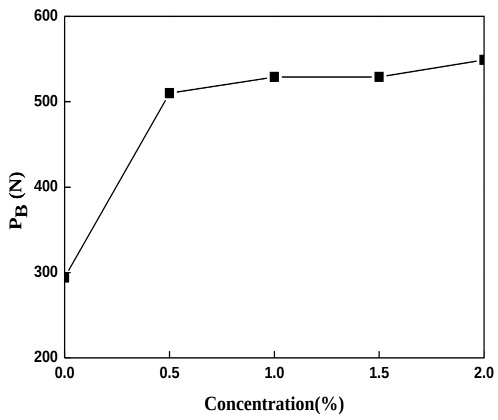


Fig. 1. The change of P_B load against the concentration

Wear Scar Diameter (WSD) represents the wear loss of the friction pair. The smaller the WSD is, the lower the wear loss is, which means the better anti-wear property. The bigger the WSD is, the higher the wear loss is, which reflects the poorer anti-wear property. Fig. 2 shows the variation of WSD with the change of the concentration on the MMW-1P universal friction & wear testing machine.

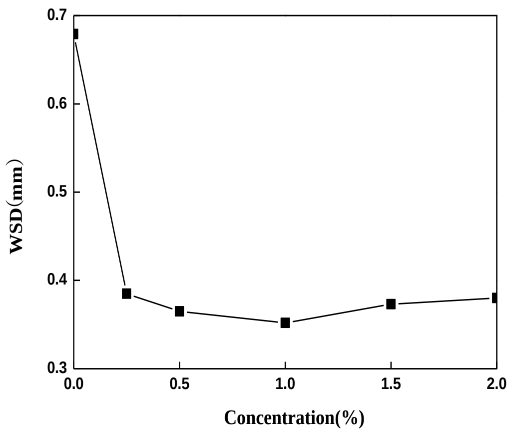


Fig. 2. The variation of WSD with the change of concentration

As seen in Fig. 2, the WSD was reduced by nearly 50%, when 0.5% lubricating additive was added into the base oil. With 1% concentration, there was a significant reduction in WSD, but it didn't vary too much with more than 1% concentration. Therefore, the most suitable concentration is 1%. The reason for this might be related to the formation of a surface film on the friction surface by the lubricating additive. When the lubricating additive are added into the base oil, it will be involved into the interaction with the freshly worn surface of the friction pair to form an adsorption film or reaction film, the shear strength of which is much lower than that of the base metal. Therefore, the adding of lubricating additive will greatly reduce WSD. However, with the increase in the concentration, the presence of an excessive number of lubricating additive molecules will affect the quality of the surface film formed by physical adsorption or chemical reaction to reduce the film strength.

3.2.2. Friction-reduction property

The change of friction coefficient against loads reflects to some extent the quality of the surface film formed during boundary lubrication. Fig. 3 and Fig. 4 separately demonstrate the change of the friction coefficient against the load when the base oil and the test oil with 1% addition were separately used for the point-contact and surface-contact lubrication of the MMW-1P universal friction & wear testing machine.

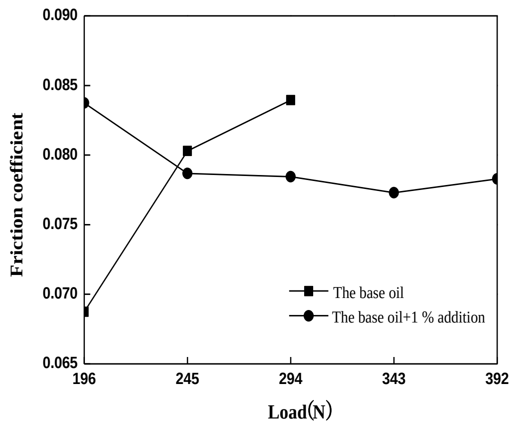


Fig. 3. The change of friction coefficient against load under point contact

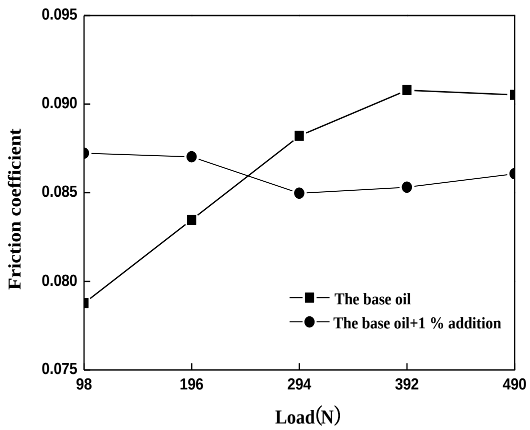


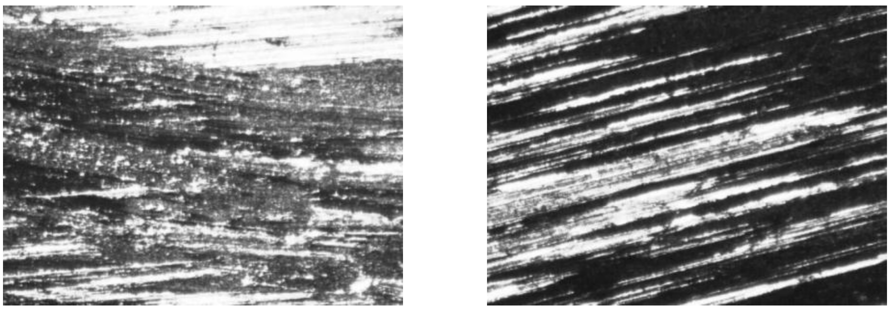
Fig. 4. The change of friction coefficient against load under surface contact

As shown in Fig. 3 and 4, the test oil with 1% addition had a higher friction coefficient than the base oil under a low load. With the increase in loads, the friction coefficient of the base oil rose as well. However, in the case of the test oil with 1% addition, the friction coefficient was reduced first and then increased. The reason for this might be that physical adsorption played a main role in the surface film under a low load. Meanwhile, in the test oil with 1% addition, competitive adsorption took place between the molecules of lubricating additive and the molecules of base oil. It would lead to the poor quality of the physical adsorption film and the increase of friction coefficient. Then with an increase in load, physical adsorption happened less frequently in the surface film of the test oil with 1% addition, while chemical adsorption occurred more often. Especially, the reaction film generated by the tribochemical reaction can enhance the strength and tenacity of the surface film to reduce the friction coefficient. Hence, with a further increase in load, the surface film was increasingly worn out and the friction coefficient rose again, but it was still obviously lower than that of the base oil under the same working condition. It shows an outstanding friction-reduction property.

3.3. Surface analysis

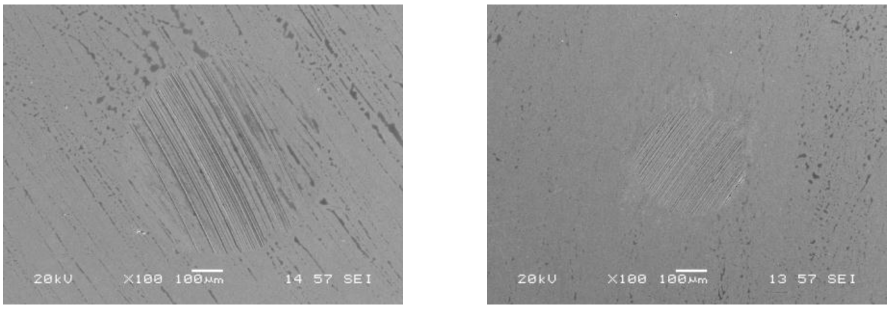
3.3.1. Analysis of surface morphology

Fig. 5 and 6 separately display the OM picture of the worn surface at every load level and the SEM picture of the wear scar morphology of the steel ball under the load of 245 with a wear time of 30 min when the base oil and the test oil with 1% addition were separately used to lubricate the MMW-1P universal friction & wear testing machine. They also reveal that under the lubrication of the test oil with 1% addition, both of the surface wear in the surface-contact tribological test and the WSD of the steel ball in the point-contact tribological test were much smaller than those under the lubrication of the base oil. All of the wear scars were shallow and had been distributed uniformly. They were mainly the fatigue wear and scuffing in the friction process. However, under the lubrication of base oil, they were mainly the adhesive and abrasive wear in the friction process.



(a) Lubricated with LP (b) Lubricated with LP + 1 %addition

Fig. 5. The OM picture (×40) of the worn surface in the surface-contact tribological test



(a) Lubricated with LP (b) Lubricated with LP + 1 %addition

Fig. 6. The SEM picture (×100) of the wear scar morphology in the point-contact tribological test

3.3.2. Analysis of surface chemical characteristics

Fig. 7 shows the XPS spectra of the Fe and N elements on the worn surface of the steel ball when the test oil with 1% addition was applied to the MMW-1P universal friction & wear testing machine under the load of 343 N with a wear time of 30 min.

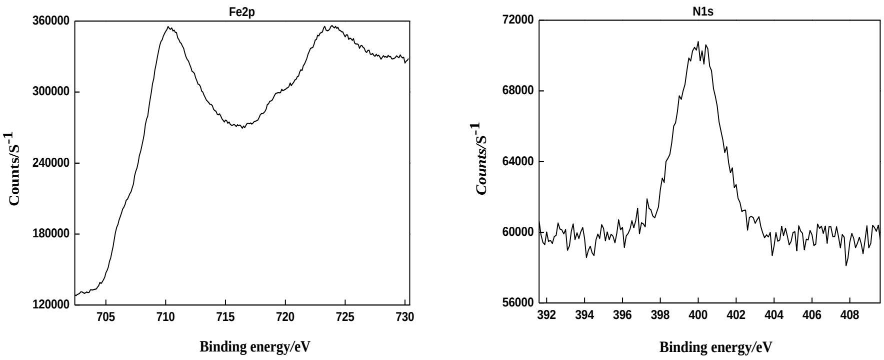


Fig. 7. The XPS spcctra(Fe_{2p} and N_{1s}) of the worn surface of the steel ball under the lubrication of the test oil with 1% addition

As revealed in Fig. 7, Fe_{2p} has an electron binding energy of 709.8 eV at the spectral peak and exists in a form of FeO on the friction surface with a weak spectral signal [16], and it proves that the wear scar surface has been covered by an effective deposited film or a tribo-chemical reaction film, which facilitates the reduction in wear loss. With an electron binding energy of 399.6 eV at the spectral peak, N_{1s} is considered as a nitrogen-containing metal complex [16], which also includes $Fe(CN)_6^{4-}$, etc. Therefore, all of these can prove that a composite surface film constituted by the product of the tribo-chemical reaction between the base oil and the lubricating additive has been generated on the worn surface of the steel ball in the friction process.

4. Conclusions

(1) A new organic nitrogen-containing heterocyclic lubricating additive without sulphur and phosphorus was prepared and characterized in this paper. With excellent anti-wear and friction-reduction performances on the commonly used steel/steel friction pair, it can not only significantly increase the maximum nonseizure load for the base oil of the analytically pure liquid paraffin (with a kinematic viscosity of 21.20 mm^2/s at 40 °C), but also greatly improve the friction and wear condition of the steel/steel friction pair to reduce the friction coefficient and wear loss.

(2) Due to the tribochemical reaction occurred in the friction process, a tribo-chemical reaction film mainly constituted by FeO and nitrogen-containing metal complexes has been formed on the friction surface of the organic nitrogen-containing heterocyclic lubricating additive. It's also a main reason for the significant improvement of the friction and wear performances of the steel/steel friction pair.

Acknowledgements

This project was funded by the Project of Technology Innovation and Application Demonstration of Chonqing (cstc2018jscx-msybX0339, cstc2017shmsA90009), Basic and Frontier Research Plan of Chongqing (cstc2017jcyjAX0146), Science and Technology Project of Chongqing Education Commission (KJQN201800822, KJZD-K201800801, KJZD-M201900802 and KJQN201800816) and Postgraduate Education Reform Project of Chongqing Technology and Business University (2016YJG0204).

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